

Ultrashort Electron Pulses

Final Report

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13. ABSTRACT (Maximum 200 words) The focus of our research is the generation of ultrashort electron pulses, and their application to time-resolved pump-probe diffraction experiments. Our diffractometer utilizes a pulsed electron source that delivers subpicosecond electron pulses. This new instrument is applied to pump-probe experiments probing molecular structures in excited states. The short duration of the laser and the electron pulses allow time-resolved experiments that follow molecular rearrangements in real time. During the funding period, significant progress has been made toward the goal of observing time resolved structures. On the experimental side, we have built a new diffractometer designed to operate with the ultrashort electron pulses. We were able to observe high quality diffraction patterns with short exposure times (seconds, rather than hours with conventional photographic plates). First test runs on pump-probe diffraction images have been performed. On the theoretical side, we continued our investigations into the observability of wave functions, and extended the theory to vibrational wave functions of diatomic and triatomic molecules. We found that the diffraction signatures of vibrational wave functions are observable with our experiment, in spite of obstacles such as orientational averaging. This opens up the opportunity to image vibrational wave functions during chemical reactions.				
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1. Statement of the problem studied

Our research explores the generation and optimization of ultrashort electron pulses, and investigates their applications to experiments that provide fundamentally new insights into properties of quantum systems.

Electron beams have found many applications in today's technology driven society. They are used in every TV and computer monitor, in night vision instruments, vacuum tubes, particle accelerators, electron microscopes, and many other devices. All these instruments utilize electron beams that are either independent of time, or very slow compared to the fastest optical pulses currently attained (<10 fs). In our research we have demonstrated, as have others, that it is possible to generate ultrashort electron pulses by ejecting electrons from a metallic surface using a picosecond or femtosecond laser pulse. The technical objective of our research is to develop a scientific and technological infrastructure that enables applications of ultrashort electron pulses as short as the fastest optical pulses. The scientific objective of our research is to explore their applications in novel scientific experiments.

Over the last 30 years, ultrashort *optical* pulses have evolved into a tremendously useful tool to study ultrafast dynamics of quantum systems in real time. It is now possible to perform time resolved spectroscopic experiments that directly reflect atomic and molecular motions, and molecular reaction processes. Critics argue that the spectroscopic results so obtained are difficult to interpret and reconcile with traditional chemists' view of chemical reactions. Nonetheless, the relevance of time-resolved spectroscopy was recognized by the Nobel Prize committee when it awarded the Nobel Prize to A. Zewail in the fall of 1999.

The difficulty of connecting ultrafast spectroscopy to chemical reaction dynamics is intrinsic in the experimental technique: spectroscopy measures energy levels and their populations. Time resolved spectroscopy observes populations as a function of time. Chemists, on the other hand, think of reactions in a structural manner: a functional group approaches some reactant from a particular side, electrostatic interactions pull them closer together, and once the reactants are in close vicinity, chemical bonds are broken and formed. Ultimately, the energy levels and the molecular structure are linked via potential energy surfaces and the Schrödinger equation, but for complicated quantum systems the link is neither intuitive nor easy to understand. And herein lies the scientific significance of the diffraction experiments that we are developing.

Diffraction experiments provide, by Fourier transformation of the diffraction pattern, a probe of the *structure* of a quantum system. Such structure determinations have been performed throughout the 20th century, and they have been perfected to the point where structures of large biomolecules can now be obtained. Our development of ultrashort electron pulses allows us to extend the measurement of diffraction patterns to include the time dimension. Conceptually, the electron pulse intersects a molecular sample at a specific time. The diffraction pattern reflects the molecular structure at the precise time when the electron interacts with the molecule. If a preceding laser pulse

excites a molecule to a transient state that undergoes a chemical reaction, then the electron pulse images the structure of the transient state. By introducing a time delay between the laser pump-pulse and the electron probe-pulse it is thus fundamentally possible to map the time dependent structure of a reacting species. Unlike spectroscopic pump-probe experiments, it is anticipated that the information obtained from pump-probe diffraction experiments is directly comparable to mechanistic reaction chemistry. Pump-probe diffraction is therefore expected to be a major milestone for modern chemistry.

Since our research explores very new territory, we pursue both an experimental and a theoretical component. The experimental work is carried out in our own laboratory, while the theoretical research is performed in part by ourselves and in part in collaboration with theorists at Brown University as well as other institutions.

Theory: While reviewing the theoretical basis of pump-probe diffraction experiments we discovered that the theoretical description of conventional diffraction experiments is not adequate to describe the patterns obtained in pump-probe diffraction experiments. We therefore developed a more general theoretical framework in which to describe pump-probe diffraction. This new theoretical formulation led to the entirely unexpected recognition that the pump-probe diffraction methodology should enable us to obtain experimental maps of probability density distributions of quantum mechanical wave functions. Since we consider this a major breakthrough that will have vast ramifications, we followed up on these thoughts with detailed theoretical investigations. Our ideas are now documented in 3 separate publications, which form the basis of a new proposal that has been submitted to ARO.

Experiments: The technological aspects of the experimental work continue to optimize the generation and propagation of ultrashort electron pulses. As outlined below, we optimized the electron pulse generation process, and the detection of two-dimensional electron diffraction patterns with a CCD camera. Diffraction experiments have been performed to optimize the diffractometer. We obtained test patterns of a variety of molecules, and worked out procedures for analyzing the patterns. Current work is directed at characterizing limits imposed by space-charge interactions between electrons within a pulse, and to assess their effect on diffraction experiments. The aim of future experiments is to explore pump-probe patterns, both with and without time resolution. Supported by theoretical model calculations, we believe that the diffraction technique is capable of providing measurements of probability density distributions. It is our goal to implement these ideas in the laboratory and demonstrate the observation of quantum mechanical wave functions of vibrational motions. These experiments are again subject of the recently submitted ARO proposal.

The milestones of both our experimental and theoretical work during the past funding period are delineated below. These milestones should be viewed as part of a multi-year effort to develop ultrafast time resolved pump-probe diffraction experiments. The ultimate goals of these experiments is to observe the time evolution of molecular structures during chemical reactions; the probability density distributions of vibrational and electronic wave functions; and the time-dependent motions of wave functions, that is wave packets, during chemical reactions.

2. Summary of the most important results

Following milestones were achieved during the funding period:

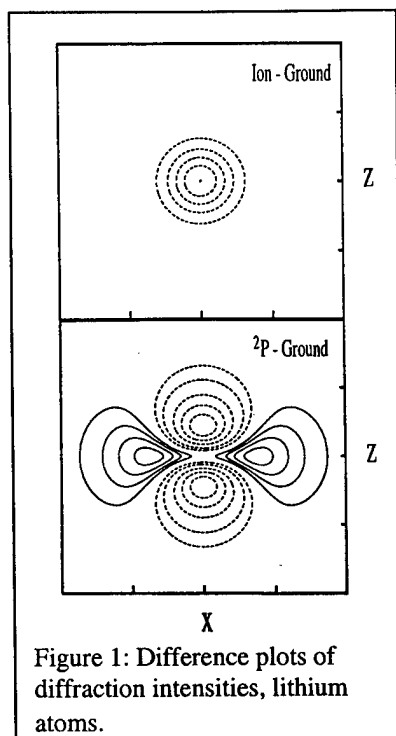
Theory

The theoretical foundation of pump-probe diffraction

At the beginning of the funding period, the PI spent 5 months on sabbatical leave with Prof. Kent Wilson at the University of California, San Diego. During this time, a thorough review of the status of the theory of diffraction experiments was performed. The result of this review was that electron diffraction theory, which had been developed to describe conventional diffraction experiments, is not applicable to pump-probe diffraction experiments.

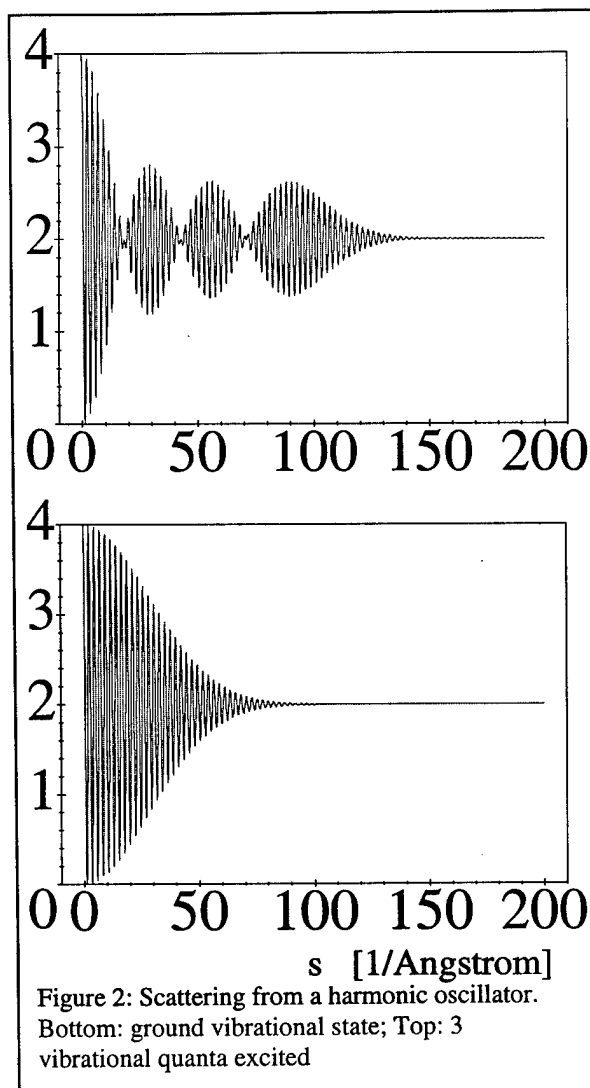
Briefly, the conventional theory describes diffraction patterns of molecules much like the diffraction of light from Young's double slit – except of course that molecules can have random orientations and multiple scattering centers. The period of the oscillations of the diffraction pattern of a double slit is inversely related to the separation of the slits. Much the same way, molecular bond lengths are obtained from the periods of the oscillations in a molecular diffraction pattern. To account for molecular vibrations, the traditional theory adds a Gaussian damping term to the diffraction patterns in an ad hoc way. This Gaussian term is quite valid for molecules in their ground vibrational states, where the wave functions have a Gaussian form. It can also be used to describe molecules in excited states, but only if the bond-lengths remain well specified. Bond lengths are, however, well defined only if the excited molecule is in a non-stationary state that is described by a sharply peaked wave packet, such as those obtained by laser excitation with extremely short pulses. If, on the other hand, the molecule is in a single vibrational state, or a superposition state made up of just a few vibrational states, then the bond length is no longer a well defined parameter. Instead, there is a probability distribution of bond lengths that is defined by the vibrational wave function. This probability distribution makes the conventional theory un-applicable to most excited states. Our extended theory deals specifically with the diffraction patterns of vibrational wave functions, and is thus able to better describe diffraction patterns observed in pump-probe experiments. Moreover, it predicts that the probability density distributions of vibrations can indeed be mapped by the diffraction experiments.

Our theoretical work opens up the fundamental possibility of directly observing wave functions during chemical reactions. Needless to say, this could be a major breakthrough for chemistry, and for this reason we directed much of our recent efforts toward the development of the theory. The results of these efforts have been published in several publications, which are briefly described below:



- The first paper of the series was written while I was still in San Diego on sabbatical leave (*Chemical Physics Letters*, **262**, 405 (1996)). In this paper we point out the fundamental observability of probability density distributions belonging to electronic wave functions, that is, orbitals. The paper develops the theory of diffraction from atomic orbitals, on the example of lithium atoms, for both x-ray and electron diffraction. As an example, the top panel of figure 1 shows the diffraction intensity of the lithium ion minus the diffraction intensity of the ground state atom. This corresponds to an experiment where the diffraction pattern is observed for the atom, and for the ion generated by ionization with a laser pulse. The difference between the patterns is largely due to the 2s electron, and the difference diffraction pattern reflects the 2s orbital. Similarly, the bottom panel shows the difference between the diffraction patterns of the atom excited to the 2P state and the ground state: this difference pattern maps largely the structure of the 2p electronic orbital. Clearly, pump-probe diffraction has the information content needed to map atomic orbitals.

Back here at Brown University, we extended the concept of mapping probability density distributions to vibrational wave functions. In a thorough analysis we showed that a pump-probe diffraction experiment (either x-ray or electron diffraction) can be used to image vibrational wave functions. As an example, figure 2 shows the



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diffraction signatures of a harmonic oscillator, in the ground vibrational state (bottom) and the $n=3$ state (top). Clearly, the diffraction signatures are extremely different, and the differences should be quite observable. This result, which originated entirely in our own group, was published in the *Journal of Chemical Physics*, (*JCP* **108**, 8004 (1998)). We consider this work a breakthrough, since it lays the foundation for many experiments exploring the static wave functions of polyatomic molecules, potential energy surfaces in polyatomic molecules, and the dynamic flow of energy through the vibrational phase space. This paper also laid the foundation for our next step.

- Clearly, the next task was to calculate diffraction patterns of polyatomic molecules. It turns out that the theoretical treatment of diffraction patterns of a polyatomic molecule is not straightforward at all. We started collaborating with theorists to help in our quest. In an initial step, we collaborated with Prof. J. Krause at the University of Florida, to theoretically model the dissociation dynamics of carbon disulfide in the S_3 electronic state. We initiated this work because carbon disulfide is an attractive candidate for the observation of wave functions, and for the probing of dissociation dynamics with the electron diffraction apparatus. Since little was known about this particular electronic surface and its dissociation dynamics, we performed theoretical calculations in collaboration with Prof. Krause. The results of this collaboration were published, *Journal of Chemical Physics*, **107**, 6570 (1997).

Building on this foundation, we extended the diffraction theory to the task of imaging molecular vibrations in carbon disulfide. We collaborated with Prof. Stratt, Brown University, on the theoretical treatment of diffraction signatures of vibrations in polyatomic molecules in general, and performed model simulations for the triatomic carbon disulfide molecule in particular. The results of these calculations are extremely encouraging: wave functions belonging to vibrational motions can be imaged with pump-probe diffraction, even in a triatomic molecule and in spite of the rotational averaging encountered in gas phase samples. Figure 3 shows the diffraction pattern of the triatomic CS_2 molecule with different amounts of excitation in the symmetric stretch coordinate, as annotated in the inset. The three panels correspond to excitation of the molecule with a laser polarized along the x-,

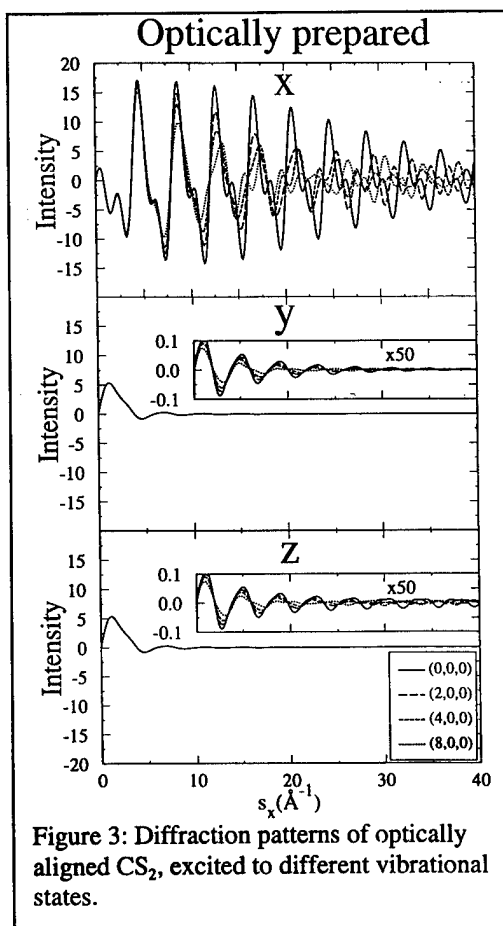


Figure 3: Diffraction patterns of optically aligned CS_2 , excited to different vibrational states.

y- and z- coordinates. The x- and y-coordinates are within the plane of the detector, while the z-coordinate is along the propagation direction of the electron beam. From this figure it is clear that the vibrational excitation profoundly alters the diffraction image in a way that enables us to map the wave function (squared). Moreover, the dependence of the effect on the alignments of laser and electron beams may ultimately offer us a handle to map the wave functions in 3 dimensions.

The final question of this work addresses the point whether the diffraction images of different vibrational states are sufficiently succinct to discern between isoenergetic vibrational state, such as those that are populated during an intramolecular vibrational relaxation process. Addressing this question, we calculated the diffraction patterns in three isoenergetic, vibrationally excited states. Figure 4 shows the state with two quanta of antisymmetric stretch (solid line), five quanta of symmetric stretch vibration (dashed line), and eight quanta of bending vibration (dotted line). Again, patterns along the x- and the z- coordinate are shown. It is evident that the patterns are very different, and for some scattering angles even completely out of phase. Thus we conclude that it is possible to image the pathway of a vibrational wave packet during an intramolecular vibrational relaxation reaction using our diffraction technique. For detailed results of this work please refer to our current publication (*Journal of Chemical Physics*, **112**, 1260, January 2000).

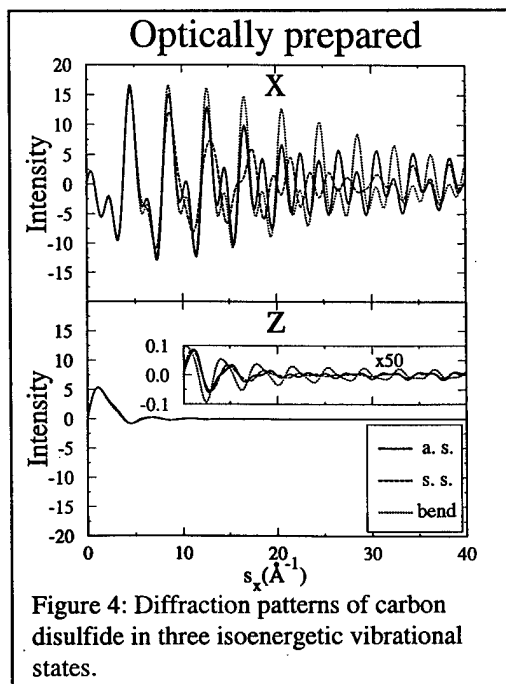


Figure 4: Diffraction patterns of carbon disulfide in three isoenergetic vibrational states.

To sum up this section, one of the most significant results of the funding period has been least anticipated. A careful review of the relevant theory led us to discover the methodology to map probability density distributions of quantum systems by performing pump-probe diffraction experiments. Recognizing the importance of this discovery, we spent great effort to develop the theory to the point where it now is applicable to vibrational wave functions of polyatomic molecules. This research has been published in major journals, and there is no doubt that it is correct. It opens the door to future experiments in which we can observe and map vibrational wave functions, and observe the changing wave functions during energy relaxation processes and chemical reactions.

Experiments

Electron pulse generation and construction of an electron diffractometer

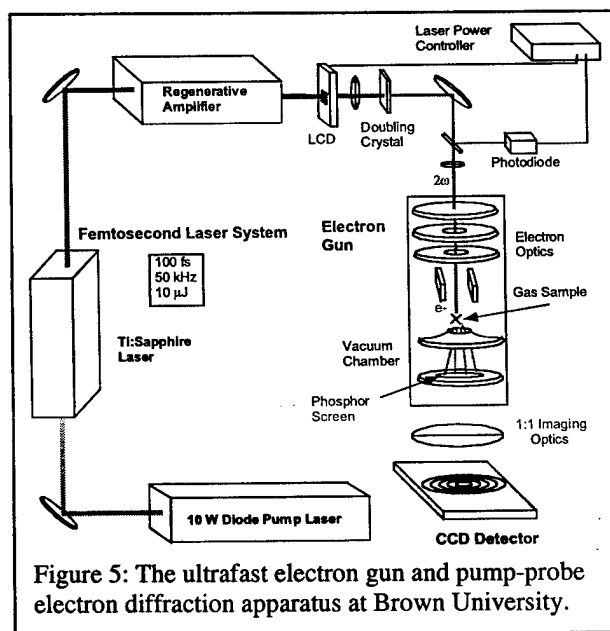
While a major thrust of our recent research has been on the theoretical development, we have completely re-built our first generation electron diffractometer during the past funding period. The two major new components are a new electron gun and a new 2-dimensional imaging system. With this new apparatus we performed comprehensive tests, and developed procedures to record and analyze diffraction patterns. Those developments are described in the next sections.

The electron gun

The ultrafast electron gun is based on the photoemission of electrons from a metallic surface by a femtosecond laser pulse, see figure 5. A ~ 80 fs duration laser pulse is generated by a regeneratively amplified Titanium Sapphire laser. The laser pulses are upconverted to about 400 nm by second harmonic generation, and projected onto a metallic photocathode.

A number of tests have been performed to find the most suitable photocathode material. To sum up what was a very significant amount of experimental work, the most obvious choice, a copper block, is also the most suitable. Soft metals, like cesium, lithium and magnesium turn out to be insufficiently stable upon laser exposure. Those metals produce large electron currents, but they last only for minutes at the high currents. Gold works as well as copper, but we found no reason to use the more expensive metal. We also tried thin layers of copper and gold, with either front or back-illumination. While those cathodes work fine as well, the thin films tend to have a lifetime of only a few months. Finally, it is worth mentioning that even a solid copper block is subject to surface damage if high laser powers are employed. This limits the maximum sustainable currents to about 2 nA, using the laser pulse train from our 50 kHz regenerative amplifier. It turns out that space-charge effects limit the usable electron beam currents more than the cathode material (see discussion below).

Using an optical imaging system (not shown in figure 5) we are able to obtain a fairly uniform illumination of a circular area on the photocathode with a diameter of



about 20 μm , and a crisp edge. Within that illuminated area electrons are ejected in a two-photon emission process. While such a process is very inefficient for picosecond laser pulses, it turns out to be quite viable with the intense femtosecond pulses that we use in our electron gun. The electrons are accelerated and focused into the interaction region by a newly constructed series of electrostatic elements. The magnification of the electrostatic lens is about 3.5x, so that the electron beam diameter in the interaction region should be about 70 μm . Tests conducted with the 80 MHz electron beam derived from the oscillator laser show that this beam diameter is indeed obtained. A reduction of the beam size to about 20 μm diameter is possible by using a platinum pinhole.

Using the electron beam derived from the 50 kHz amplified laser we found that such small beam diameters are only obtained for the smallest electron beam currents (≤ 30 pA). Larger currents lead to a blooming of the electron beam to a diameter of 500 μm or larger. We trace this blooming to space-charge interactions between the electrons within a pulse, most likely near the photocathode where the electron velocities are still small. We are currently in the process of characterizing the space-charge interactions and assessing their effect on pump-probe diffraction experiments.

The 2-dimensional detector

Funding by ARO allowed us to develop a new 2-dimensional imaging system that is based on a liquid-nitrogen cooled CCD camera. Most electron diffractometers to date still operate with photographic plates. While this seems quaint and antiquated, it turns out that photographic plates are astonishingly well suited for diffraction work. They are very sensitive, linear over a very wide dynamic range, and can have a large area. Unfortunately, they are not suited for pump-probe diffraction experiments, because images need to be quickly processed and subtracted from other images. We therefore developed a CCD based imaging detector. A phosphor screen or YAG scintillator crystal captures the electron diffraction pattern: under exposure to an electron beam both emit a greenish glow. A very fast (f/1.2) lens system images the diffraction pattern onto a liquid nitrogen cooled CCD chip. We use a 512 x 512 pixel chip with a 12.7 mm x 12.7 mm size.

We measured the quantum efficiency of the complete detector to be 18%. That is, a single electron hitting onto the scintillator is converted to a CCD-count with a probability of 0.18. This compares favorably to a non-imaging detector, such as a photomultiplier, or the direct illumination of a CCD. Typical quantum efficiencies of PMT's are about 10 to 20%, and directly illuminated CCD's have efficiencies of 20 to 50%, depending on the particle energy. (They do, however, get damaged by such exposures.) Thus, our optical system is able to provide high quality imaging with hardly a loss of sensitivity, while preserving the integrity of the expensive CCD chip.

The 16 bit CCD has a readout noise of about 5 counts, which limits our dynamic range to $2^{16}/5 \approx 13,000$. This dynamic range is necessary, but adequate for the observation of diffraction patterns. This point is demonstrated in figure 6 and 7, as well as figures 8 and 9 below. Figure 6 shows a simulation of the total diffraction signal expected for the CCl_4 molecule. The intensity of the scattered diffraction signal decreases very rapidly with increasing scattering angle. This rapid decay largely reflects the decrease in the atomic

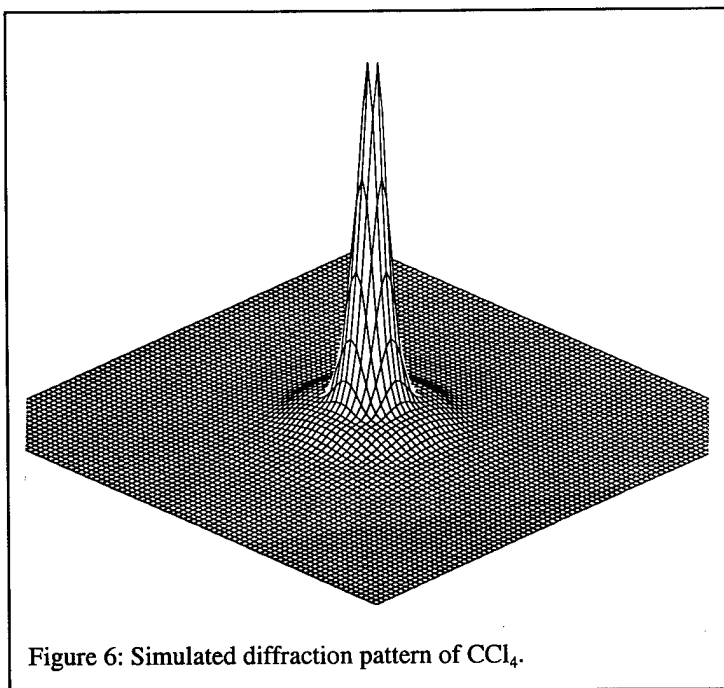


Figure 6: Simulated diffraction pattern of CCl_4 .

scattering factors, and it contains no information about the molecular structure. The structural information is contained in the modulations that are superimposed on the rapid decay. Those modulations are barely perceptible in figure 6. Any detector suitable for diffraction experiments must be able to follow these modulations over a fair range of diffraction angles. This requires that the detector not saturate at the central part of the pattern, and still have good signal to noise at the outer fringes.

Shown in Figure 7 is our observed diffraction pattern of CCl_4 , taken with a 20 s exposure time. While the central part appears saturated in this print-out, on the computer it is clear that we do not saturate our detector. (The maximum count rate is $2^{16} = 65,536$, while the scale on this graph is from 0 to 7,000.) We also note that we can observe diffraction signal out to the edges of the CCD chip. Clearly, our new detector is very well suited for diffraction work.

Development of procedures for obtaining pump-probe diffraction patterns

One of the challenges of electron diffraction is that the fringes that contain the information about atom-atom distances are not always easy to see in the diffraction patterns. The CCl_4 pattern shown in figures 6 and 7 is somewhat of a best case, because the large symmetry of the molecule results in many identical atom-atom distances. Most patterns show an intensity that decays almost uniformly with increasing scattering angle; the 'almost' is, of course, where the molecular structure information is embedded.

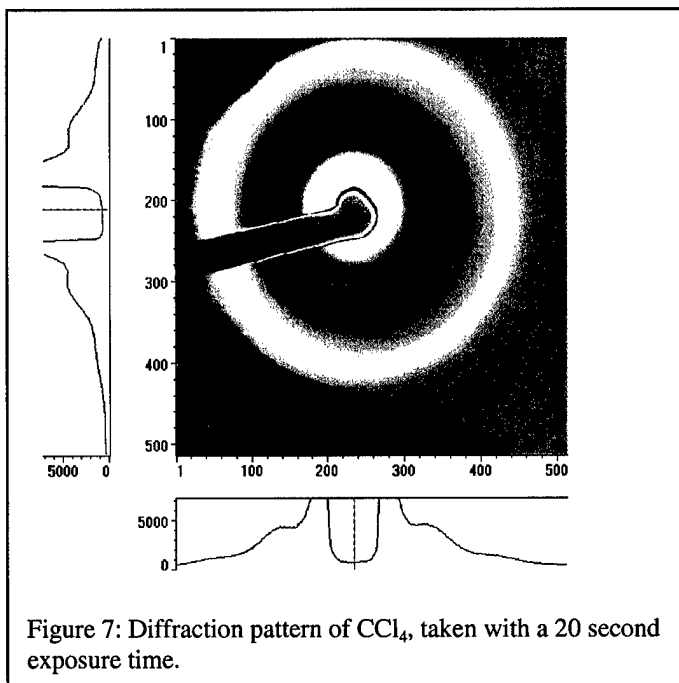


Figure 7: Diffraction pattern of CCl_4 , taken with a 20 second exposure time.

We have developed a convenient method to emphasize the diffraction rings that are buried within the rapidly decaying cone of the diffraction patterns. Our procedure has the advantage that it can be implemented in the laboratory, and that it takes only minutes. Figure 8 shows a pattern of CCl_4 that is obtained from figure 7 by first subtracting out the dark counts, and then dividing the pattern of by an experimental pattern of argon, which is easy to obtain and featureless. Even though the decay of the atomic scattering signal of argon differs from that of either carbon or chlorine, we find that diffraction rings are readily emphasized by this procedure. (The asymmetry in the difference pattern is due to a drift of the laser beam; see discussion below.) While of course this procedure does not change any information content of the

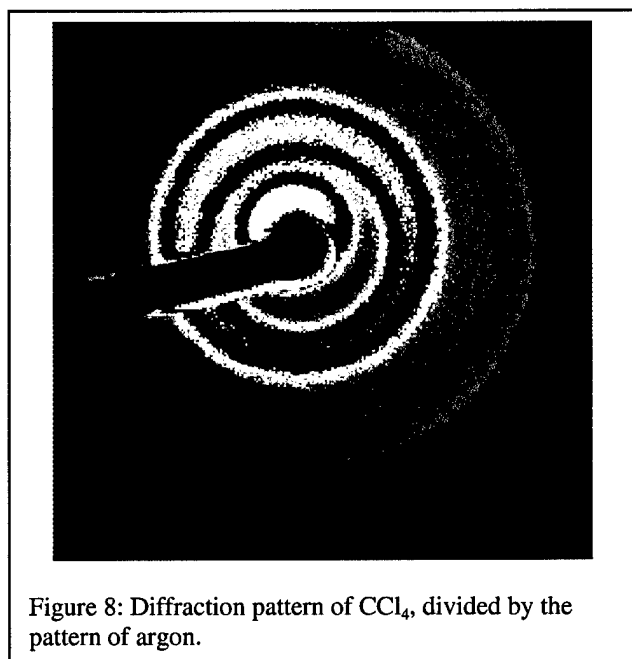


Figure 8: Diffraction pattern of CCl_4 , divided by the pattern of argon.

diffraction pattern, it is extremely convenient to see the fringes in the laboratory when optimizing the diffractometer alignment. As such, this procedure affords us a convenient and reliable alignment methodology that enables us to efficiently search for difference signals.

Tests of difference patterns

In pump-probe diffraction patterns we will observe the difference between a laser-excited molecule and the same molecule in the ground state. To simulate this situation, we took diffraction patterns of two different gases, oxygen and nitrogen, with their respective pressures adjusted to give about equal diffraction signals. (For either of those gases, the fringes arising from molecular scattering are not visible in the diffraction images without extensive data analysis.) We then subtracted the patterns arising from those two molecules. Since the bond lengths are not quite equal, 1.208 Å in oxygen vs. 1.098 Å in nitrogen, one should expect to observe oscillations in the difference pattern.

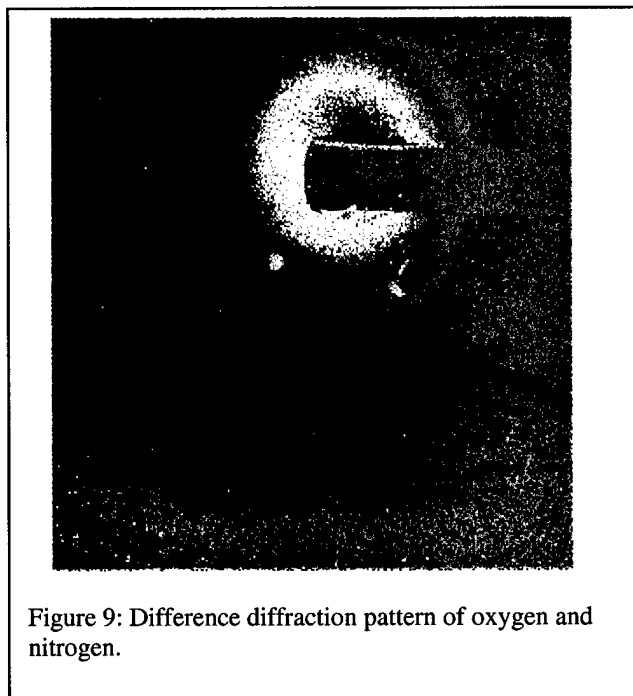


Figure 9: Difference diffraction pattern of oxygen and nitrogen.

As illustrated in figure 9, we indeed do observe such fringes. This demonstrates that our diffractometer is able to observe difference patterns, and that our analysis procedures are adequate to pull these fringes out of the steep cones of the atomic scattering signal. Most importantly, it demonstrates that the dynamic range of our detector is sufficient to record the difference patterns over a large range in scattering angles.

Status of the electron diffraction experiments and challenges that lie ahead

Electron diffraction experiments on gaseous samples are very difficult experiments. Nonetheless, we have solved many of the technical challenges and are now in a position where we can generate ultrashort electron pulses, propagate them through a vacuum apparatus, and use them to record high quality diffraction images with reasonably short exposure times and large dynamic range. We can do this on a routine

basis on any molecule with sufficient vapor pressure. And we have learned to analyze the data in such a way as to emphasize the diffraction fringes while eliminating the uninteresting parts arising from purely atomic scattering.

The challenge that still lies ahead is to record pump-probe diffraction images of laser excited molecules: we want to measure a diffraction image of a laser-excited molecule, and subtract it from a pattern of a molecule in its ground state. Progress has been made in recording pump-probe diffraction patterns, but our results have not yet been reproducible enough to warrant their dissemination. We identified two sources of problems: the stability of the lasers and space-charge effects.

For most of the past funding period our efforts to record pump-probe patterns have been severely affected by an insufficiently stabilized argon ion laser. In fact, the laser tube died in the winter of 1999 and had to be replaced. Instead of replacing the tube, however, we were able to purchase a new diode pumped laser. This was made possible by re-budgeting the existing ARO funds, and through a generous support of our research by Brown University. The new laser was delivered in the spring of 1999. It operates beautifully, although in July of 1999 we experienced 3 weeks of down-time due to a failure of one of the diode banks. With this problem solved, we are now in the process to try the pump-probe diffraction measurements again.

To record the change in the diffraction patterns induced by laser excitation it is important that a reasonably large fraction of the molecules be excited to a higher state. Given the energy of the pulses from our 50 kHz laser system (about 0.4 μ J at the third harmonic, 270 nm), we need to focus the pump laser to a spot diameter of about 20 μ m in order to obtain a 10% probability of molecular excitation. That is easily possible; however, the electron beam needs to be of similar diameter. We noted above that, using platinum apertures, the electron optics is capable of delivering beam diameters in that range, as tested with the 80 MHz electron beam. However, when we use the 50 kHz electron beam we observe a space-charge induced blooming of the spot diameter for currents in excess of 30 pA. This blooming makes the electron beam diameter so large that pump-probe diffraction patterns are difficult to obtain. We are presently addressing this issue and explore solutions to it. One solution might be to increase the exposure times while keeping the electron currents small. (This puts additional burden on the stability of the lasers.) Another might be to slightly lengthen the duration of the electron pulses so as to increase the average separations between electrons. Finally, a further amplification of our pump laser system would allow us to operate with larger electron beam diameters, which would enable us to accept the adverse effects of the space-charge interactions. We note that the future experiments exploring the mapping of vibrational probability distributions can very well be conducted on a picosecond time scale, where space-charge interactions are expected to be significantly diminished. For those experiments an amplified picosecond laser system might be more appropriate than our femtosecond laser.

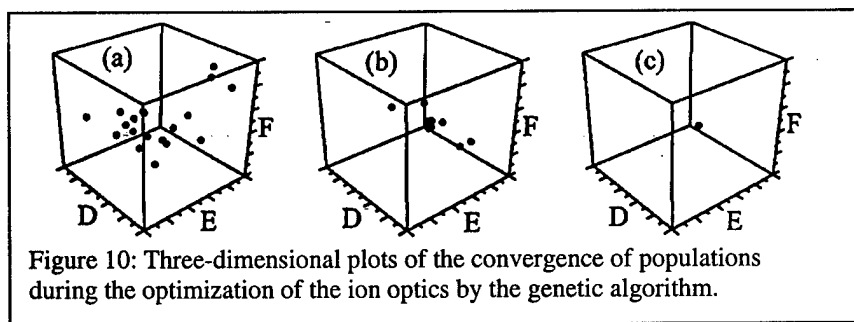
Related experiments: Adaptive and Quantum Control

As part of our exploration of novel techniques to study molecules we have an ongoing interest in the quantum control of molecular systems. While past funding levels have not allowed us to be a major player in this field as well, we were able to contribute some significant advances to the field of quantum control.

Early on we realized that a successful implementation of quantum control on complex systems requires an adaptive learning algorithm that is able to optimize many experimental parameters in the presence of noise, and use feedback from the molecular system to optimize the control of the molecule. Thus, one of my students, Scott Carpenter, spent 3 months in Hungary to learn about genetic algorithms. Back at Brown, he implemented a genetic algorithm into an apparatus to shape femtosecond laser pulses. In the spring of 1997, Scott worked in the laboratory of our collaborator Kent Wilson at the University of California in San Diego. He transferred the technology of genetic algorithms to San Diego, and used it to shape the 20 fs pulses of their kilohertz laser system. Using this laser system with the adaptive learning algorithm we were able to demonstrate quantum control on the dye IR 125 in methanol solution. For details please see our publication in *Chemical Physics Letters*, **280**, 151, (1997).

With Scott Carpenter back at Brown, we decided to explore the limits of experimental implementation of genetic learning algorithms in a laboratory by investigating the optimization of a many-dimensional space in the presence of experimental noise. We optimized a mass spectrometer by allowing the genetic algorithm to optimize the 8 voltages of an ion optics assembly. We found that the genetic algorithm was able to enhance the detection efficiency of the instrument by a factor of 10, and the mass resolution by a factor of 11, compared to previous settings that had been derived from computer simulations of the ion trajectories. The success of the genetic

algorithm to find a global maximum in the optimization of the mass resolution is illustrated in figure 10. Shown are scatter plots of the convergence of populations. The three axes



correspond to 3 out of the 8 ion optic voltages optimized by the algorithm. Each member of the population is represented by a point in the 3-D space spanned by the voltages. It can be seen that at the beginning of the optimization, different members of the populations have widely different voltage settings (panel (a)). As the program optimizes the mass resolution the population converges (panel (b)), until it converges at the global maximum (panel (c)). This experiment highlights the utility of genetic algorithms in optimizing real-live instruments with many adjustable parameters. For more details about this work please see our paper in *Rev. Sci. Instr.*, **70**, 2262, (1999).

Conclusion

The past funding period has been very busy and productive for us. We are confident that we used the funds given to us by ARO wisely, and that we leveraged them in a way that allowed us to be optimally productive. As a result we can proudly look at a total of 14 publications within the last 3 years. More importantly, we believe that our publications are not run-off-the-mill. Instead, they represent new science that we developed in very creative ways, covering a very large range of the most important areas of chemical physics. As such, the genetic algorithm papers provide a very essential piece in the puzzle of controlling the behavior of quantum systems. The theoretical demonstration of the fundamental ability of pump-probe diffraction experiments to map quantum mechanical probability density distributions is a major development that will carry ample fruit. And, we made great progress in the implementation of the ultrafast pump-probe diffraction technology in our laboratory. We are grateful to ARO for providing us the opportunity to serve science with such marvelous results.

3. Complete list of manuscripts submitted and published under ARO sponsorship, during the funding period.

"Femtosecond Three-Photon Ionization of Phenol: evidence for a Superexcited Molecular State," with C. P. Schick; submitted for publication.

"The Diffraction Signatures of Individual Vibrational Modes in Polyatomic Molecules," with S. Ryu and R. M. Stratt; *J. Chem. Phys.* **112**, 1260, (2000).

"Femtosecond Multi-Photon Ionization Photoelectron Spectroscopy of the S_2 State of Phenol," with S. D. Carpenter and C. P. Schick; *J. Phys. Chem. A*, **103**, 10470 (1999).

"Experimental Adaptive Optimization of Mass Spectrometer Ion Optic Voltages Using a Genetic Algorithm;" with S. D. Carpenter and C. P. Schick; *Review of Scientific Instruments*, **70**, 2262 (1999).

"Feedback Quantum Control of Population Transfer Using Shaped Femtosecond Pulses;" with C. J. Bardeen, V. V. Yakovlev, K. R. Wilson, S. D. Carpenter, and W. S. Warren; in *Ultrafast Phenomena XI*, eds. T. Elsaesser, J. G. Fujimoto, D. Wiersma and W. Zinth. Berlin: Springer-Verlag, (1998).

"New Ways to Observe and Control Dynamics" K. R. Wilson, C. J. Bardeen, C. P. J. Barty, G. J. Brakenhoff, A. H. Buist, J. Cao, S. D. Carpenter, J. Che, D. N. Fittinghoff, M. Müller, J. A. Squier, W. S. Warren, P. M. Weber, V. V. Yakovlev; In *Laser Techniques for Condensed-Phase and Biological Systems*, eds. N. Scherer and J. M. Hicks, Proceedings of SPIE--the International Society for Optical Engineering, 3273. Bellingham, WA: SPIE, p. 214, (1998).

"Pump-probe diffraction imaging of vibrational wave functions" With J. D. Geiser; *J. Chem. Phys.* **108**, 8004 (1998).

"Structure and Dynamics of the S_3 state of CS_2 " With R. T. Sadeghi, S. R. Gwaltney, J. L. Krause, and R. T. Skodje. *J. Chem. Phys.* **107**, 6570 (1997).

"Feedback Quantum Control of Molecular Electronic Population Transfer" With C. J. Bardeen, V. V. Yakovlev, K. R. Wilson, Scott D. Carpenter, and W. S. Warren. *Chem. Phys. Lett.* **280**, 151 (1997).

"Ultrafast x-ray diffraction and absorption." With C. P. J. Barty, M. Ben-Nun, T. Guo, F. Ráksi, C. Rose-Petruck, J. Squier, K. R. Wilson, V. Yakovlev, Z. Jiang, A. Ikhlef and J. C. Kieffer, in *"Time resolved electron and x-ray diffraction"*, Eds. P. M. Rentzepis and J. Helliwell, Oxford University Press, New York, (1997).

"Time-resolved surface electron diffraction." With H. E. Elsayed-Ali, in *"Time resolved electron and x-ray diffraction"*, Eds. P. M. Rentzepis and J. Helliwell, Oxford University Press, New York, (1997).

"Direct imaging of Excited Electronic States using Diffraction Techniques: Theoretical Considerations" With M. Ben-Nun, Todd J. Martinez and K. R. Wilson. *Chem. Phys. Lett.* **262**, 405 (1996).

"Sub-20-fs multiterawatt laser and ultrafast x-ray source." With C. P. J. Barty, T. Guo, C. LeBlanc, F. Ráksi, C. Rose-Petruck, J. A. Squier, B. Walker, K. R. Wilson, V. V. Yakovlev, and K. Yamakawa; in *"Ultrafast Phenomena X"*, Eds. J. Fujimoto, W. Zinth, P. F. Barbara and W. H. Knox, Springer Verlag, Berlin, p. 77 (1996).

"Extended operation of a wide-range, all magnetic bearing turbomolecular pump without backing" With J. R. Thompson, and R. Hellmer. *J. Vac. Sci. Technol. A* **14** (5), 2965, (1996).

4. List of participating scientific personnel

Graduate students who participated in the research project :

Ray Dudek: Electron Diffraction; anticipated to graduate in 2000.

Carolyn Schick: Photoelectron Spectroscopy; graduation: May 2000.

Scott Carpenter: Graduated May 1999; Experimental adaptive optimization with genetic algorithms: Solving problems in mass spectrometry, optics, photoelectron spectroscopy, and quantum control." Scott is currently a post-doc at MIT.

John Thompson: Graduated May 1998; Thesis: "Pump-probe low energy electron diffraction." John is currently a post-doc at the University of Washington.

Joseph Geiser: Graduated May 1998; Thesis: "Pump-probe gas phase electron diffraction." Joe was a post-doc at Cornell University with Prof. Paul Houston, and is now on the Chemistry faculty at the University of New Hampshire .

Undergraduate students participating in our research:

Conor L. Evans: Since January 1999.

Raju Goyal: Since summer 1998. Raju will graduate in Spring of 2000, and is currently applying to graduate schools.

Xenia Amashukeli: graduated in 1997; now a graduate student at Cal Tech.

Kevin Kubarych: graduated in 1996; now a graduate student at the University of Toronto.

Michelle Silva: graduated in 1996; now a graduate student at MIT.